Supporting information for

Molecular Origin of the Glass Transition in Polyelectrolyte Assemblies

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Experimental and Simulational Procedures

Materials. Poly(diallyldimethylammonium chloride) (PDADMAC, 20 wt % in water, Sigma Aldrich, M_w = 200 000−350 000 g·mol^{-1}) and poly(sodium 4-styrenesulfonate) (PSS, Scientific Polymer Products, M_w = 500 000 g·mol^{-1}) were used as received. Polyelectrolyte solutions were prepared using deionized water with 18.2 MΩ·cm resistivity. Sodium chloride (EMD Chemicals Inc.) was added to the polyelectrolyte solution to adjust the ionic strength.

Preparation of polyelectrolyte complexes and multilayers. The homopolymer solutions of PDADMAC and PSS were prepared at 50 mM concentration with respect to their repeat unit. The concentration of the salt in the polyelectrolyte solution was adjusted to 0, 0.1, 0.5, 1.0 and 1.5 M by adding NaCl. The polyelectrolyte complexes (PECs) were prepared by mixing stoichiometric amounts of PDADMAC and PSS solutions under stirring. The precipitate PECs were centrifuged at 10000 rpm for 10 min, pressed at 6000 psi pressure using Carver Press, and quickly rinsed with copious water. After being dried in a convection oven at 343 K overnight, the PECs were ground into fine powders. The powders were intensively dried in vacuum at 423 K for 6 h and sealed in a container until further characterization.

The preparation of polyelectrolyte multilayers (PEMs) were described in previous work.[1] The PEMs were assembled in 0.5 M NaCl solution.

The PEC or PEM structure is considered a physical network, with polycation-polyanion pairs (intrinsic ion pairs) acting as physical crosslinks. Salt doping disrupts the intrinsic ion pairs and converts them into polyion−counterion pairs (extrinsic ion pairs), which increases polymer mobility.[2,3] Salt doping of the PEC may be described according to the following equation:

$$\mathrm{Pol^{+}Pol^{-}{+}Na^{+}{+}Cl^{-}} \rightleftharpoons \mathrm{Pol^{+}Cl^{-}{+}Pol^{-}Na^{+}} \quad (S1)$$

Further, the molar ratio of salt to polymer repeat unit (assuming that the PEC has stoichiometric composition) is defined as the salt doping level,[4] shown in the equation:

$$y = \frac{[\mathrm{NaCl}]}{[\mathrm{Pol^{+}Pol^{-}}]} = \frac{[\mathrm{Cl^{-}}]}{[\mathrm{Pol^{+}}]} = \frac{[\mathrm{Na^{+}}]}{[\mathrm{Pol^{-}}]} \qquad (S2)$$

Neutron activation analysis (NAA). NAA is a highly sensitive and well developed nuclear technique for multi-elemental quantification purposes. It has been shown to be an accurate detection method of counterions or metal elements in polymeric materials. [5-8] The basic theory is described briefly as follows. The various isotopes of elements in the sample capture neutrons when exposed to a steady flux of thermal neutrons for a period of time, forming compound nuclei at excited states. The activated nuclei instantaneously de-excite into a more stable configuration, radioisotopes in most of the cases, by rapid emission of gamma rays (photons). The subsequent delayed gamma radiation generated by the radioisotopes can be utilized for detection and identification of the elements.[9] Transfer of the PEC powder, weighing from 20 to 40 mg, into irradiation containers was carried out in a nitrogen glovebox to avoid moisture absorption. The samples were irradiated in a 1 MW TRIGA reactor for 30 s at a neutron flux of 9.1×10^{12} $\mathrm{n\cdot cm^{-2}\cdot s^{-1}}$ and cooled for intervals of 270 s and up to 1 to 3 h. The subsequent gamma-ray photons were counted using a high-purity Ge (HPGe) gamma-ray detector. The Na, Cl and S mass fractions were quantified using multiple gamma-ray emissions from the decay of ^{24}Na, ^{38}Cl, and ^{37}S, respectively.

NAA detection of Na, Cl, and S elements were used for calculating the composition of the PECs. While the amount of sulfur atoms S is a sign of PSS fraction in the system, two assumptions were made to calculate the PDADMA mol%: (1) The dried PEC powder samples were assumed to be electroneutral. The number of negatively charged groups or ions was equal to the number of positively charged ones: $\mathrm{PSS^{-} + Cl^{-} = PDADMA^{+} + Na^{+}}$. (2) All $\mathrm{Na^{+}}$ and $\mathrm{Cl^{-}}$ ions were assumed to be associated with the charged groups of the polyelectrolyte chains. This means, the $\mathrm{Na^{+}}$ and $\mathrm{Cl^{-}}$ ions are assumed to form extrinsic ion pairs with the polyelectrolyte and not NaCl crystals in the PECs. Notably, the sample here is solid powder instead of aqueous suspension.

Proton nuclear magnetic resonance spectroscopy. Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) (500 MHz proton frequency, Varian Inova 500 spectrometer) was employed to measure the composition of the PECs. 30 mg dried PEC sample was dissolved in 0.7 mL 2.5 M KBr in D_2O in a NMR tube. The NMR spectra of PDADMAC, PSS, and PEC were used to calculate the composition of the PECs. The D_2O peak was chosen as the reference at 4.79 ppm.[10] The PEC composition is calculated by comparing the integration of NMR peak areas of the 4 aromatic hydrogens of PSS (between 5.5 and 9 ppm) and the 16 aliphatic hydrogens of PDADMAC and 3 of PSS (between 0 and 4.6 ppm).[11]

Modulated differential scanning calorimetry. Modulated DSC (Q200, TA Instruments) was performed on PECs and PEMs in both dried and hydrated states. Dried PEC powder was loaded in a Tzero pan and covered with Tzero lid. Hydrated samples were prepared by adding water into the PEC powder using a microliter syringe dropwise until required mass was reached. The pan was subsequently sealed with a Tzero hermetic lid and rested for at least 24 h. The water content was varied from 16 to 32 wt % at intervals of 2 wt %. For PEMs hydrated samples, 0.1 M or 0.5 M KBr solutions was used to hydrate PEM samples. Modulated DSC was performed on samples in a heat-cool-heat-cool cycle. The samples were ramped from 278 K to 413 K at a rate of 2 K·min^{-1} with amplitude of 1.272 K for a period of 60 s. Nitrogen was used as a purge gas at 50 mL·min^{-1}. The T_g was taken as the inflection point of the second heating cycle, unless otherwise stated. No unexpected or unusually high safety hazards were encountered.

Molecular dynamics simulations. All-atom molecular dynamics (MD) simulations of assemblies consisting of 42-44 PDADMA$_{20}$ and PSS$_{20}$ molecules, where the subscript 20 refers to the number of repeat unit in each chain, were performed using the Gromacs 5.1.3 package[12,13] and the OPLS-aa force field.[14,15] The precise number of polyelectrolyte chains depends on the salt concentration. Sodium and chloride ion parameters were from Ref.[16,17] and PSS partial charges from Ref.[18]. Water was modelled by the explicit TIP4P water model.[19] Electrostatics were described by the PME method.[20] Temperature control was by the V-rescale thermostat[21] and pressure control at reference pressure 1 bar by the Parrinello-Rahman barostat[22] with coupling constants 0.1 ps and 2 ps, respectively. Van der Waals interactions employed a 1.0 nm cut-off.

Throughout the simulations, all the bonds in the polyelectrolytes and water molecules were controlled by the LINCS [23] and SETTLE [24] algorithms, respectively. A 2 fs (initially 0.5 fs) time step within the leap-frog integration scheme was applied and the trajectories were written every 1000 steps. The polyelectrolytes were coupled to the heat bath as one thermostatting group while water and the ions were coupled to the heat bath as another group.

The chemical structures of polyelectrolytes and sample chain fragment conformations are presented in Figure S1. The initial configurations were generated using PACKMOL[25], with polyelectrolyte chain conformations extracted from dilute solution. The detailed steps of obtaining polyelectrolytes assemblies with relatively uniform structure and water distribution are presented in the Table S1. The generated initial configurations were simulated for 100 ns in an elevated 370 K temperature after which the temperature was brought down to 290 K in 10 ns time as the relaxation before the production run. System compositions reflect the compositions determined experimentally using neutron activation analysis as closely as reasonably feasible. Modelled assembly compositions correspond to 0, 0.5, and 1.5 M NaCl preparation solutions. For each NaCl concentration, hydrations of 22, 26, and 30 wt % water were studied. The ions wt % and PSS to PDADMA ratio (based on repeat unit molar ratio) in each simulation are gathered in the Table S2 and the detailed simulation compositions in the Table S3.

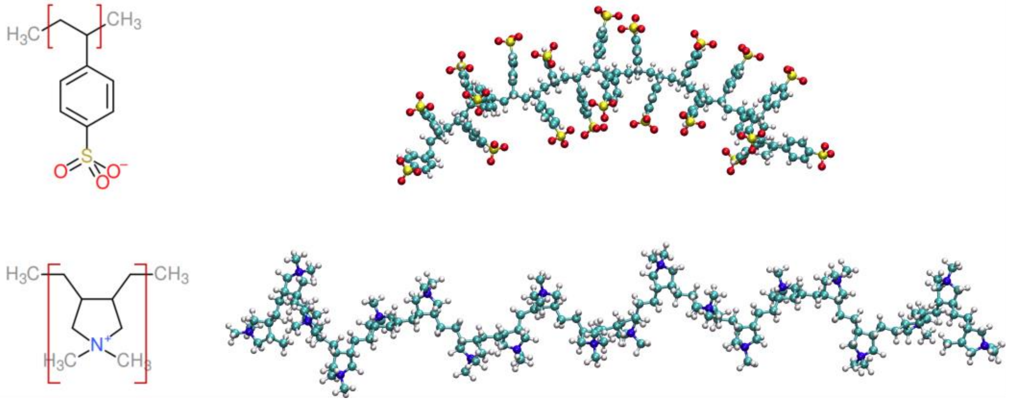

Figure S1. The chemical structures of the examined polyelectrolytes and snapshots of the structures from molecular dynamics simulations. PSS$^-$ is at the top panel and PDADMA$^+$ at the bottom.

Table S1. Molecular dynamics simulation protocol

No.	**Ensemble**	**Duration [ns]**	**Time step [fs]**	**Temperature [K]**	**Simulation box**	**Comments**
1	NVT	1	0.5	290	20x20x20 nm	Initial hydration of the PEs with position restraints applied on the PE chains (prevents PE-PE bonding without water shell)
2	NPT	0.5	0.5	290	Isotropic pressure coupling	Initial box size relaxation (short time step because of significant compression of the box to reach approximately 1 bar pressure)
3	NPT	50	2	370		Equilibration in elevated temperature
4	NPT	50	2	370	Anisotropic pressure coupling (off-diagonal compressibilities set to zero to keep box rectangular)	Continuation of the equilibration in elevated temperature with a more flexible simulation box
5	NPT	10	2	Linear cooling ramp from 370 K		Relaxation

				to 290 K during the first 6 ns. Then 290 K.		
6	NPT	225	2	Stepwise temperature ramping from 290 K to 360 K with 5 K increase steps. 15 ns simulation at each step.		Production run

Table S2. Composition of the PECs in the simulations and experiments. The experimental PEC composition is based on the neutron activation analysis as discussed in detail in the Results section.

	0M		0.5M		1.5M	
	Experi-ments	Simula-tions	Experi-ments	Simula-tions	Experi-ments	Simula-tions
Na^+ [wt%]	0.012	0.00	0.382	0.350	1.56	1.54
Cl^- [wt%]	0.91	1.04	2.54	2.69	3.35	3.37
PSS to PDADMA ratio	0.922	0.913	0.833	0.826	0.922	0.913

Table S3. Composition of the simulated systems. The NaCl concentration refers to the experimental assembly process.

Molecule type		**0M NaCl**	**0.5M NaCl**	**1.5M NaCl**
		Number of molecules		
PSS$_{20}$		21	19	21
PDADMA$_{20}$		23	23	23
Na^{+}		0	20	95
Cl^{-}		40	100	135
Water	**22 wt%**	2138	2064	2225
	26 wt%	2664	2571	2772
	30 wt%	3250	3137	3382

The initial configurations were generated using PACKMOL.[25] In the production run, the temperature was increased from 290 K to 360 K in 5 K steps of 15 ns each for a total simulation duration of 215 ns. The first 1 ns of each temperature step was disregarded in the analysis. The presented results correspond to the average of three different initial configurations, unless otherwise stated. The employed timescale is too short to capture polymer chain relaxation and diffusion but water and ion dynamics are captured. All simulations employ periodic boundary conditions. Visualizations were done by the VMD software.[26]

For hydrogen bond analysis, a 0.35 nm cut-off distance and 30º angle was used. The cut-off corresponds to the minimum after the first peak in the corresponding radial distribution function (RDF) (Figure S2). A PSS monomer is defined as extrinsically compensated if a Na^{+} ion is within a cut-off separation of 0.45 nm from the PSS S atom and intrinsically compensated otherwise. The ion pairing classification was conducted at the beginning of the production run at 290 K. The ion pairing did not change significantly during the temperature ramping which implied that the simulation time scale is insufficient to capture polyelectrolyte chain motion.

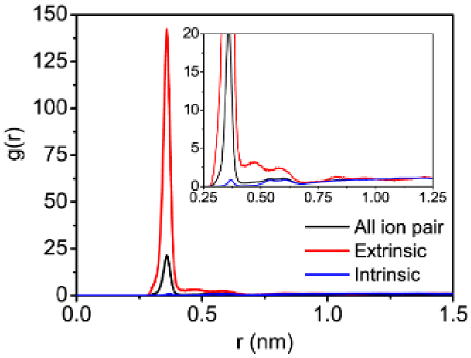

Figure S2. Radial distribution function calculated from the molecular dynamics simulations between the S atom in PSS group and Na^+ ion in PECs with 22 wt % water and prepared from 0.5M NaCl.

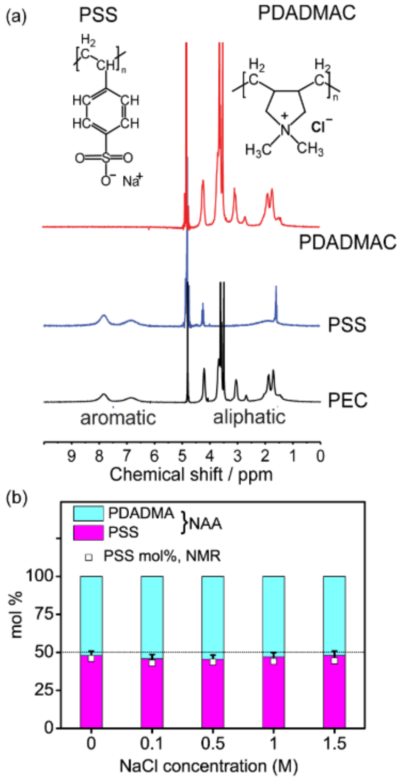

Figure S3. (a) ^1H NMR spectra for homopolymer PDADMAC, PSS, and PDADMA−PSS complexes in 2.5 M KBr in D_2O, (b) PEC composition based on PDADMA and PSS repeat units for PECs prepared at varying NaCl concentrations measured using NAA or NMR. The PSS mol % (by repeat unit) was found to be ca. 43 to 46 % in various samples, in line with the NAA analysis.

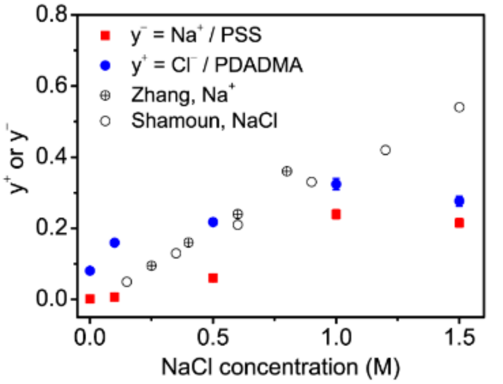

Figure S4. Comparison of current work and previous work on salt doping level of PDADMAC−PSS complexes. Doping levels, for which y^- and y^+ are the molar ratios of Na^+ to PSS and Cl^- to PDADMA, respectively. Work from Zhang et al.,[27] detection of Na^+ (⊕) using inductively coupled plasma mass spectrometry (ICP-MS), and Shamoun et al.,[28] detection of NaCl (○) using solution conductivity.

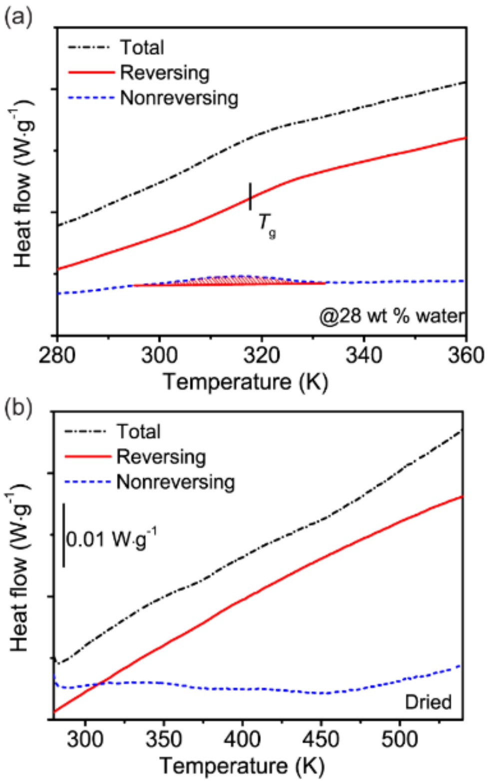

Figure S5. Modulated DSC thermograms of (a) 28 wt % hydrated and (b) dried PDADMA−PSS complexes isolated from 0.5 M NaCl. Second heating scans were shown here with "exotherm down" format. Heating at 2 K·min^{-1}, amplitude of 1.272 K for a period of 60 s. Curves have been shifted along y-axis for clarity.

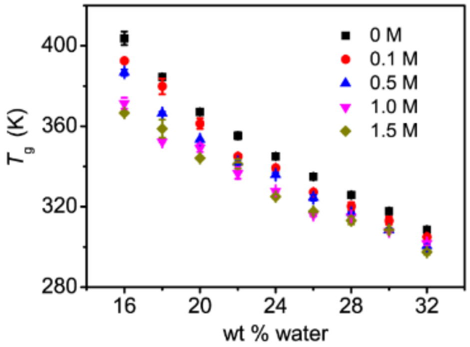

Figure S6. T_g values for PDADMA−PSS complexes of varying complexation NaCl concentration and hydration. The error bars represent the standard error of 3 samples.

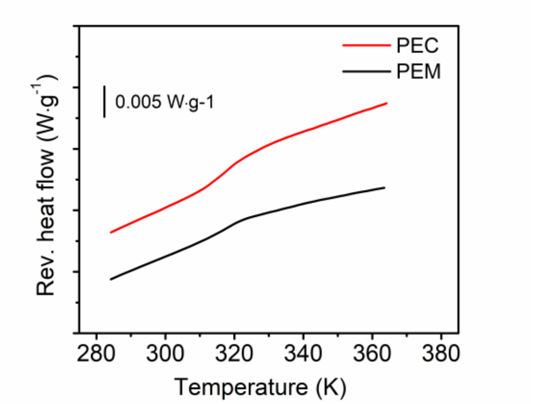

Figure S7. First reversing heat flow curves for PDADMA−PSS complexes (PECs) and multilayers (PEMs). PEC is made at 0.5 M NaCl, hydration level 28 wt% and the PEM is made at 0.5 M NaCl, hydration level 26.5 wt%. First heating scans are shown with “exotherm down”, heating at 2 K·min^{-1}, amplitude of 1.272 K for a period of 60 s.

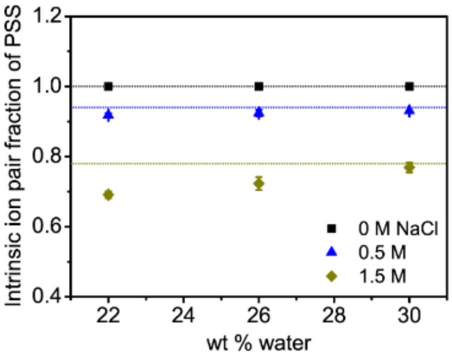

Figure S8. (Solid data points) Calculated intrinsic ion pair fraction of PSS groups from simulation work; (dashed lines) experimental values from ion pairing model of PECs. The simulation produces a relatively realistic configuration as 3D packing. The experimental results were obtained from simpler 2D configuration. At 0 and 0.5 M NaCl complexation conditions, the results obtained from simulations matches the experimental results. At higher salt concentration of 1.5 M, counterions are insufficiently solvated, i.e. at high salt doping and low hydration, and the simulation values exceed experimental ones.

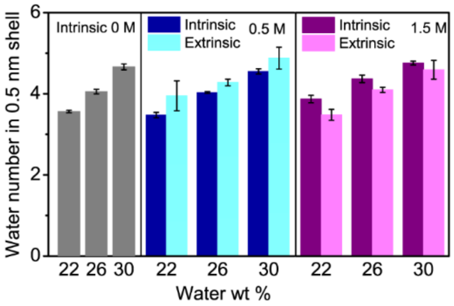

Figure S9. Number of water molecules in the first hydration shell of PSS in hydrated PECs prepared from complexation solutions of varying NaCl concentration. No clear trend on the number of water as the function of the specific salt doping level was observed. The 0.5 nm shell corresponds to the first hydration shell, and thus could underestimate the number of molecules associated with the site. When comparing number of water in intrinsic and extrinsic ion pairs, the differences were below 13%, although water was not evenly distributed between intrinsic and extrinsic ion pairs.

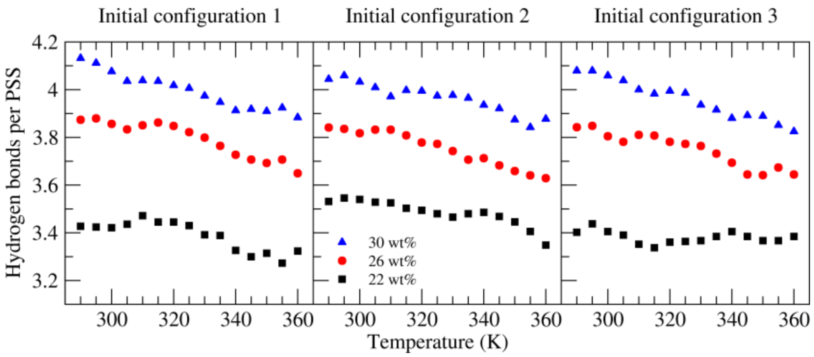

Figure S10. The number of intrinsically compensated PSS−water hydrogen bonds for individual simulation runs of PECs with different water content prepared from 0.5 M NaCl solution.

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